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4-Nitrophenylhydrazinium picrate monohydrate

Hong-lan Cai,* Bing Liu and Qing-an Qiao

School of Chemistry and Material Science, Ludong University, Yantai 264025, People's Republic of China

Correspondence e-mail: honglan_cai@126.com

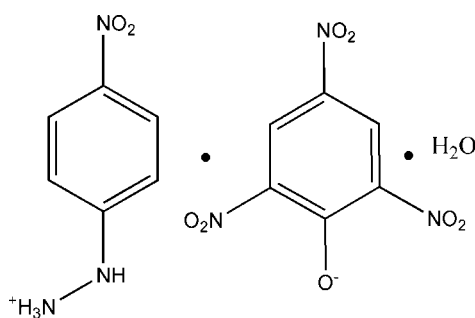
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Key indicators: single-crystal X-ray study; $T = 299$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.063; wR factor = 0.150; data-to-parameter ratio = 13.4.

In the crystal structure of the title compound, $\text{C}_6\text{H}_8\text{N}_3\text{O}_2^{+}\cdot\text{C}_6\text{H}_2\text{N}_3\text{O}_7^{-}\cdot\text{H}_2\text{O}$, $\text{N}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds link the components into a two-dimensional network parallel to (010). In addition, there are pairs of weak inversion-related $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds within the two-dimensional network. The three nitro groups are twisted by 1.6 (3), 7.8 (3) and 12.1 (3)° from the ring plane in the anion, while in the cation, the nitro group makes a dihedral angle of 4.6 (2)° with the ring.

Related literature

For the use of picric acid as a co-crystallization agent, see: Herbststein & Kaftory (1976); Dubost *et al.* (1981); Harrison *et al.* (2007); Peng *et al.* (2011); Zeng *et al.* (2011); Dey *et al.* (2011).



Experimental

Crystal data

$\text{C}_6\text{H}_8\text{N}_3\text{O}_2^{+}\cdot\text{C}_6\text{H}_2\text{N}_3\text{O}_7^{-}\cdot\text{H}_2\text{O}$
 $M_r = 400.28$
 Monoclinic, $P2_1/c$
 $a = 4.8483$ (3) Å
 $b = 28.798$ (2) Å

$c = 11.6352$ (8) Å
 $\beta = 101.360$ (1)°
 $V = 1592.70$ (18) Å³
 $Z = 4$
 Mo $K\alpha$ radiation

$\mu = 0.15$ mm⁻¹
 $T = 299$ K

0.20 × 0.08 × 0.04 mm

Data collection

Bruker SMART CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 1997)
 $T_{\min} = 0.971$, $T_{\max} = 0.994$
 16632 measured reflections
 3643 independent reflections
 2487 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.045$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.063$
 $wR(F^2) = 0.150$
 $S = 1.05$
 3643 reflections
 271 parameters
 10 restraints

H atoms treated by a mixture of independent and constrained refinement

$\Delta\rho_{\text{max}} = 0.31$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.31$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H1A}\cdots\text{O10}^i$	0.87 (1)	2.05 (1)	2.916 (3)	177 (2)
$\text{N1}-\text{H1B}\cdots\text{O10}$	0.87 (1)	1.94 (1)	2.809 (3)	172 (2)
$\text{N1}-\text{H1B}\cdots\text{O9}^{ii}$	0.87 (1)	2.56 (3)	2.908 (3)	105 (2)
$\text{N1}-\text{H1C}\cdots\text{O6}^{iii}$	0.87 (1)	2.08 (1)	2.947 (3)	170 (2)
$\text{N2}-\text{H2A}\cdots\text{O4}$	0.86 (1)	2.13 (2)	2.868 (3)	144 (3)
$\text{O10}-\text{H10A}\cdots\text{O3}$	0.82 (1)	2.09 (2)	2.832 (3)	150 (3)
$\text{O10}-\text{H10A}\cdots\text{O4}$	0.82 (1)	2.24 (2)	2.743 (3)	120 (2)
$\text{O10}-\text{H10B}\cdots\text{O3}^{ii}$	0.83 (1)	2.05 (1)	2.869 (3)	171 (3)
$\text{O10}-\text{H10B}\cdots\text{O9}^{ii}$	0.83 (1)	2.43 (3)	2.898 (3)	117 (3)
$\text{C11}-\text{H11}\cdots\text{O8}^{iv}$	0.93	2.51	3.433 (3)	172

Symmetry codes: (i) $x - 1, y, z$; (ii) $-x + 1, -y + 1, -z + 1$; (iii) $x - 1, y, z - 1$; (iv) $-x + 3, -y + 1, -z + 2$.

Data collection: SMART (Bruker, 2001); cell refinement: SAINT-Plus (Bruker, 2001); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: PLATON (Spek, 2009); software used to prepare material for publication: SHELXTL (Sheldrick, 2008).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH5673).

References

- Bruker (2001). SAINT-Plus and SMART. Bruker AXS Inc., Madison, Wisconsin, USA.
 Dey, S. K., Pramanik, A. & Das, G. (2011). *CrystEngComm*, **13**, 1664–1675.
 Dubost, J.-P., Léger, J.-M., Hickel, D. & Colleter, J.-C. (1981). *Acta Cryst.* **B37**, 751–754.
 Harrison, W. T. A., Swamy, M. T., Nagaraja, P., Yathirajan, H. S. & Narayana, B. (2007). *Acta Cryst.* **E63**, o3892.
 Herbststein, F. H. & Kaftory, M. (1976). *Acta Cryst.* **B32**, 387–396.
 Peng, Y., Zhang, A.-J., Dong, M. & Wang, Y.-W. (2011). *Chem. Commun.* **47**, 4505–4507.
 Sheldrick, G. M. (1997). SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
 Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
 Zeng, B., Li, J. & Wang, G. (2011). *Acta Cryst.* **E67**, o1464.

supporting information

Acta Cryst. (2014). E70, o15 [https://doi.org/10.1107/S1600536813032479]

4-Nitrophenylhydrazinium picrate monohydrate

Hong-lan Cai, Bing Liu and Qing-an Qiao

S1. Comment

Cocrystal strategy has been often used due to its application in the fields of drug chemistry, physical material chemistry and biological crystallography. Picric acid, as a strong organic acid, is very frequently adopted to facilitate the crystallization of some difficult-crystallized organic bases (Herbstein & Kaftory, 1976; Dubost *et al.*, 1981; Harrison *et al.*, 2007; Peng *et al.*, 2011; Zeng *et al.*, 2011; Dey *et al.*, 2011). In this report, we report the 1:1 cocrystallized complex of 4-nitrophenylhydrazine and picric acid in 95% methanol solution.

In the title compound (I), the asymmetric unit consists of a 4-nitrophenylhydrazinium cation, a picrate anion and a solvent water molecule (Fig.1). During the preparation of (I) the picric acid proton has been transferred to the terminal hydrazine atom N1. In the picrate molecule, the phenolate (O3—C7) bond distance is 1.245 (3) Å shows an indication of delocalization between the precursor single C—O bond and the benzene ring with three electron-withdrawing nitro groups. As a result, the neighbouring C7—C8 and C7—C12 bond lengths of 1.459 (3) Å and 1.452 (3) Å are longer by *ca* 0.08 Å than the mean distance of the other four C—C bonds. The C8—C7—C12 angle is about 10° smaller than the mean value (121.4°) of the other five benzene inner angles. The three nitro groups N4/O4/O5, N5/O6/O7 and N6/O8/O9 are twisted by 1.6 (3)°, 7.8 (3)° and 12.1 (3)° from the picrate benzene ring plane, respectively.

In the crystal, N—H···O and O—H···O hydrogen bonds link the components of the structure into a two-dimensional network parallel to (010) (Fig. 2). In addition, there are pairs of weak inversion related C—H···O hydrogen bonds within the two-dimensional network.

S2. Experimental

All the reagents and solvents were used as obtained without further purification. 1:1 molar amount of 4-nitrophenylhydrazine (0.2 mmol, 30.6 mg) and picric acid (0.2 mmol, 45.8 g) were dissolved in 95% methanol (20.0 ml). The mixture was stirred for half an hour at ambient temperature and then filtered. The resulting yellow solution was kept in air for one week. Yellow needles of (I) suitable for single-crystal X-ray diffraction analysis were grown by slow evaporation of the solution at the bottom of the vessel. The crystals were filtered and dried in air. Yield: 60.2 mg, 75% (based on picric acid or 4-nitrophenylhydrazine).

S3. Refinement

H atoms bonded to C atoms were positioned geometrically with C—H = 0.93 Å (aromatic) and refined in a riding-model approximation with [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{aromatic C})$]. H atoms bonded to N and O atoms were found in difference Fourier maps and refined with the constraints of N—H = 0.86 (1) Å and O—H = 0.82 (1) Å. The N1-bonded H···H distances were constrained by using the SADI command in SHELXL (Sheldrick, 2008). The water O10-bonded H···H distance was constrained to be 1.35 (1) Å. The isotropic displacement parameters of of N-bonded and water O10-bonded hydrogen atoms were set 1.2 times and 1.5 times of their parent atoms, respectively.

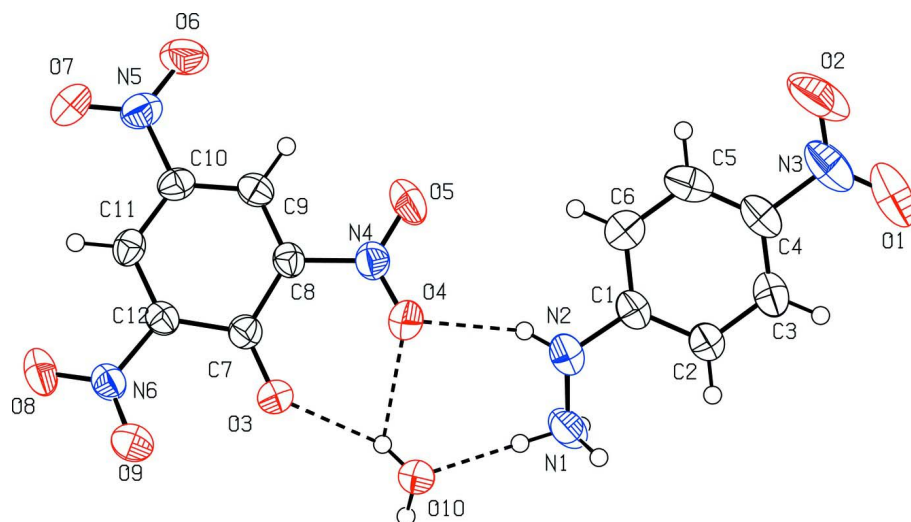


Figure 1

Molecular structure of (I) showing displacement ellipsoids drawn at the 50% probability level. H-bonds are shown in dashed lines.

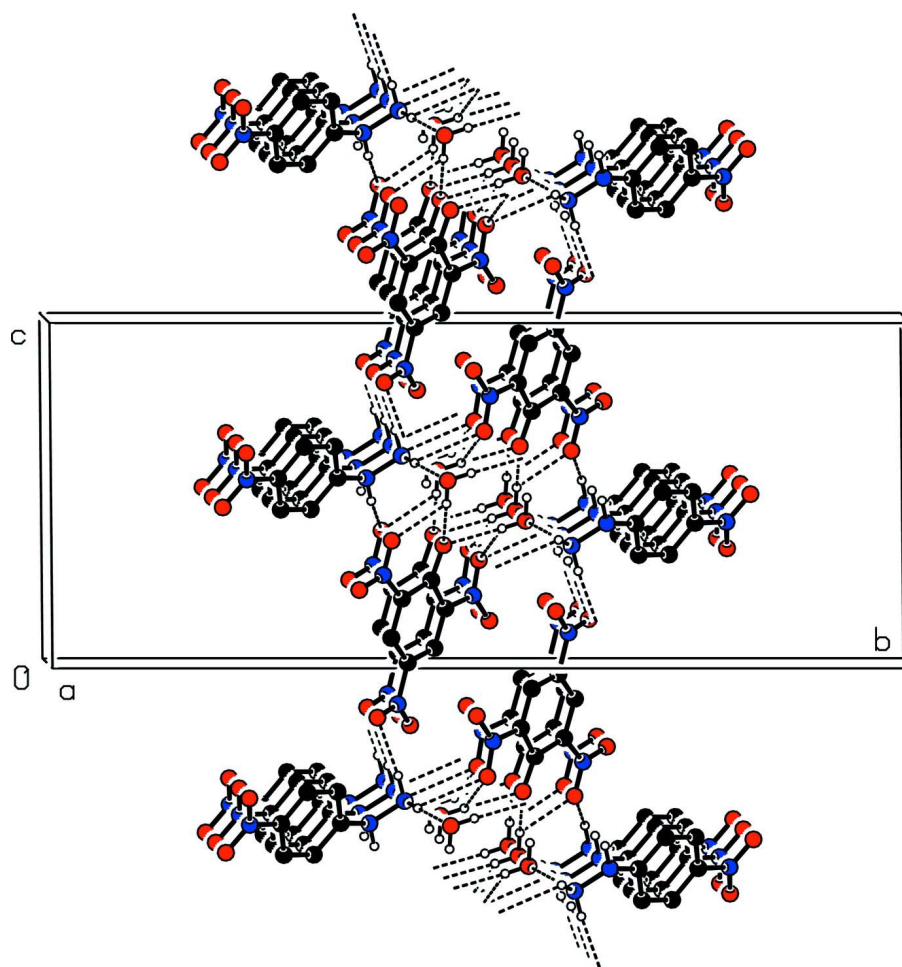


Figure 2

Part of the crystal structure of (I) showing the formation of a two-dimensional network parallel to (010). Hydrogen bonds are shown as dashed lines. For the sake of clarity, H atoms not involved in the motif have been omitted.

4-Nitrophenylhydrazinium picrate monohydrate

Crystal data

$C_6H_8N_3O_2^+ \cdot C_6H_2N_3O_7^- \cdot H_2O$

$M_r = 400.28$

Monoclinic, $P2_1/c$

Hall symbol: $-P 2ybc$

$a = 4.8483$ (3) Å

$b = 28.798$ (2) Å

$c = 11.6352$ (8) Å

$\beta = 101.360$ (1)°

$V = 1592.70$ (18) Å³

$Z = 4$

$F(000) = 824$

$D_x = 1.669$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 924 reflections

$\theta = 2.3$ – 21.5 °

$\mu = 0.15$ mm⁻¹

$T = 299$ K

Needle, yellow

$0.20 \times 0.08 \times 0.04$ mm

Data collection

Bruker SMART CCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator
 φ and ω scans

Absorption correction: multi-scan
(*SADABS*; Sheldrick, 1997)
 $T_{\min} = 0.971$, $T_{\max} = 0.994$
16632 measured reflections
3643 independent reflections
2487 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.045$
 $\theta_{\text{max}} = 27.5^\circ$, $\theta_{\text{min}} = 1.9^\circ$
 $h = -6 \rightarrow 6$
 $k = -37 \rightarrow 36$
 $l = -14 \rightarrow 15$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.063$
 $wR(F^2) = 0.150$
 $S = 1.05$
3643 reflections
271 parameters
10 restraints
Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map
Hydrogen site location: inferred from
neighbouring sites
H atoms treated by a mixture of independent
and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0602P)^2 + 0.5955P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.31 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.31 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	-0.3571 (5)	0.67096 (8)	0.4377 (2)	0.0427 (6)
C2	-0.5710 (5)	0.67706 (9)	0.3408 (2)	0.0473 (6)
H2	-0.5922	0.6562	0.2786	0.057*
C3	-0.7524 (6)	0.71420 (9)	0.3368 (3)	0.0523 (7)
H3	-0.8968	0.7186	0.2722	0.063*
C4	-0.7169 (6)	0.74447 (8)	0.4294 (3)	0.0505 (7)
C5	-0.5048 (7)	0.73915 (10)	0.5256 (3)	0.0603 (8)
H5	-0.4836	0.7603	0.5870	0.072*
C6	-0.3246 (6)	0.70235 (10)	0.5302 (3)	0.0555 (7)
H6	-0.1806	0.6983	0.5952	0.067*
C7	0.7836 (5)	0.56180 (8)	0.7388 (2)	0.0365 (5)
C8	0.6275 (5)	0.59770 (7)	0.7872 (2)	0.0344 (5)
C9	0.6776 (5)	0.61004 (7)	0.9025 (2)	0.0361 (5)
H9	0.5682	0.6327	0.9287	0.043*
C10	0.8913 (5)	0.58870 (8)	0.9798 (2)	0.0375 (5)
C11	1.0603 (5)	0.55567 (8)	0.9429 (2)	0.0363 (5)
H11	1.2063	0.5420	0.9960	0.044*
C12	1.0107 (5)	0.54316 (7)	0.8270 (2)	0.0345 (5)

N1	-0.2290 (5)	0.59509 (8)	0.3776 (2)	0.0543 (6)
H1A	-0.377 (3)	0.5818 (9)	0.394 (2)	0.065*
H1B	-0.078 (3)	0.5783 (8)	0.399 (2)	0.065*
H1C	-0.250 (4)	0.6027 (10)	0.3037 (11)	0.065*
N2	-0.1620 (5)	0.63550 (8)	0.4446 (2)	0.0579 (6)
H2A	-0.069 (6)	0.6290 (11)	0.5132 (14)	0.070*
N3	-0.9135 (7)	0.78313 (9)	0.4265 (3)	0.0711 (8)
N4	0.3991 (4)	0.62195 (7)	0.71219 (19)	0.0419 (5)
N5	0.9370 (5)	0.60035 (8)	1.10213 (19)	0.0481 (5)
N6	1.2004 (4)	0.50850 (7)	0.79502 (19)	0.0403 (5)
O1	-1.1132 (6)	0.78583 (8)	0.3443 (3)	0.0885 (8)
O2	-0.8693 (7)	0.81070 (9)	0.5084 (3)	0.1111 (11)
O3	0.7262 (4)	0.54803 (7)	0.63542 (15)	0.0569 (5)
O4	0.3387 (6)	0.61246 (9)	0.6108 (2)	0.1019 (10)
O5	0.2717 (6)	0.65136 (10)	0.7518 (2)	0.0989 (10)
O6	0.7656 (5)	0.62597 (7)	1.13576 (17)	0.0648 (6)
O7	1.1385 (5)	0.58370 (8)	1.16900 (17)	0.0676 (6)
O8	1.3571 (5)	0.48802 (8)	0.87253 (19)	0.0694 (6)
O9	1.2022 (4)	0.50150 (8)	0.69233 (18)	0.0697 (6)
O10	0.2853 (4)	0.54747 (6)	0.43546 (16)	0.0545 (5)
H10B	0.264 (7)	0.5203 (5)	0.413 (2)	0.082*
H10A	0.362 (7)	0.5483 (10)	0.5049 (12)	0.082*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0376 (13)	0.0414 (13)	0.0506 (15)	0.0074 (10)	0.0123 (11)	0.0029 (11)
C2	0.0436 (14)	0.0457 (14)	0.0508 (15)	0.0078 (11)	0.0049 (12)	-0.0036 (12)
C3	0.0426 (15)	0.0480 (15)	0.0648 (18)	0.0083 (12)	0.0067 (13)	0.0059 (14)
C4	0.0498 (15)	0.0353 (13)	0.0716 (19)	0.0075 (11)	0.0248 (14)	0.0055 (13)
C5	0.074 (2)	0.0456 (15)	0.066 (2)	0.0037 (14)	0.0243 (17)	-0.0121 (14)
C6	0.0565 (17)	0.0579 (17)	0.0494 (16)	0.0044 (13)	0.0038 (13)	-0.0049 (13)
C7	0.0354 (12)	0.0358 (12)	0.0376 (13)	0.0002 (10)	0.0059 (10)	-0.0009 (10)
C8	0.0320 (11)	0.0294 (11)	0.0407 (13)	-0.0004 (9)	0.0041 (10)	0.0015 (9)
C9	0.0375 (12)	0.0301 (11)	0.0423 (14)	-0.0018 (9)	0.0120 (10)	-0.0013 (10)
C10	0.0440 (13)	0.0336 (12)	0.0346 (13)	-0.0063 (10)	0.0069 (10)	-0.0033 (9)
C11	0.0354 (12)	0.0349 (12)	0.0363 (13)	-0.0043 (10)	0.0011 (10)	0.0038 (10)
C12	0.0321 (12)	0.0303 (11)	0.0413 (13)	-0.0012 (9)	0.0081 (10)	-0.0009 (9)
N1	0.0623 (15)	0.0477 (13)	0.0567 (15)	0.0216 (12)	0.0210 (12)	0.0058 (11)
N2	0.0523 (14)	0.0538 (14)	0.0629 (16)	0.0191 (11)	-0.0006 (12)	-0.0046 (12)
N3	0.077 (2)	0.0415 (14)	0.105 (2)	0.0169 (13)	0.0438 (18)	0.0148 (15)
N4	0.0409 (11)	0.0384 (11)	0.0444 (13)	0.0028 (9)	0.0040 (9)	0.0026 (9)
N5	0.0614 (14)	0.0457 (12)	0.0366 (12)	-0.0035 (11)	0.0087 (11)	-0.0022 (10)
N6	0.0341 (10)	0.0359 (10)	0.0500 (13)	0.0014 (8)	0.0067 (9)	-0.0026 (9)
O1	0.0673 (15)	0.0633 (15)	0.140 (2)	0.0261 (12)	0.0334 (16)	0.0306 (15)
O2	0.149 (3)	0.0583 (15)	0.135 (3)	0.0392 (16)	0.052 (2)	-0.0139 (16)
O3	0.0600 (12)	0.0658 (12)	0.0397 (10)	0.0221 (10)	-0.0030 (9)	-0.0134 (9)
O4	0.128 (2)	0.0933 (18)	0.0613 (15)	0.0675 (16)	-0.0387 (14)	-0.0269 (13)

O5	0.0998 (19)	0.121 (2)	0.0703 (16)	0.0799 (17)	0.0031 (13)	-0.0105 (15)
O6	0.0896 (16)	0.0642 (13)	0.0453 (11)	0.0148 (11)	0.0250 (11)	-0.0069 (9)
O7	0.0718 (14)	0.0810 (15)	0.0410 (11)	0.0095 (11)	-0.0104 (10)	-0.0080 (10)
O8	0.0686 (13)	0.0686 (13)	0.0667 (14)	0.0360 (11)	0.0026 (11)	0.0090 (11)
O9	0.0672 (13)	0.0888 (16)	0.0532 (13)	0.0298 (12)	0.0125 (10)	-0.0155 (11)
O10	0.0654 (13)	0.0531 (11)	0.0411 (11)	0.0203 (10)	0.0008 (9)	-0.0079 (9)

Geometric parameters (Å, °)

C1—N2	1.384 (3)	C10—N5	1.437 (3)
C1—C2	1.385 (4)	C11—C12	1.371 (3)
C1—C6	1.391 (4)	C11—H11	0.9300
C2—C3	1.380 (4)	C12—N6	1.454 (3)
C2—H2	0.9300	N1—N2	1.403 (3)
C3—C4	1.370 (4)	N1—H1A	0.866 (10)
C3—H3	0.9300	N1—H1B	0.873 (10)
C4—C5	1.371 (4)	N1—H1C	0.874 (10)
C4—N3	1.462 (3)	N2—H2A	0.857 (10)
C5—C6	1.367 (4)	N3—O1	1.222 (4)
C5—H5	0.9300	N3—O2	1.227 (4)
C6—H6	0.9300	N4—O4	1.190 (3)
C7—O3	1.245 (3)	N4—O5	1.193 (3)
C7—C12	1.452 (3)	N5—O7	1.221 (3)
C7—C8	1.459 (3)	N5—O6	1.231 (3)
C8—C9	1.362 (3)	N6—O8	1.212 (3)
C8—N4	1.448 (3)	N6—O9	1.213 (3)
C9—C10	1.376 (3)	O10—H10B	0.825 (10)
C9—H9	0.9300	O10—H10A	0.820 (10)
C10—C11	1.378 (3)		
N2—C1—C2	122.3 (2)	C12—C11—H11	120.4
N2—C1—C6	117.6 (2)	C10—C11—H11	120.4
C2—C1—C6	120.0 (2)	C11—C12—C7	124.0 (2)
C3—C2—C1	119.7 (3)	C11—C12—N6	115.8 (2)
C3—C2—H2	120.1	C7—C12—N6	120.2 (2)
C1—C2—H2	120.1	N2—N1—H1A	111 (2)
C4—C3—C2	119.1 (3)	N2—N1—H1B	102 (2)
C4—C3—H3	120.4	H1A—N1—H1B	112.3 (15)
C2—C3—H3	120.4	N2—N1—H1C	108 (2)
C3—C4—C5	121.9 (2)	H1A—N1—H1C	112.3 (15)
C3—C4—N3	119.1 (3)	H1B—N1—H1C	110.8 (15)
C5—C4—N3	119.0 (3)	C1—N2—N1	119.9 (2)
C6—C5—C4	119.3 (3)	C1—N2—H2A	116 (2)
C6—C5—H5	120.3	N1—N2—H2A	111 (2)
C4—C5—H5	120.3	O1—N3—O2	123.9 (3)
C5—C6—C1	119.9 (3)	O1—N3—C4	118.6 (3)
C5—C6—H6	120.0	O2—N3—C4	117.5 (3)
C1—C6—H6	120.0	O4—N4—O5	120.0 (2)

O3—C7—C12	124.0 (2)	O4—N4—C8	119.8 (2)
O3—C7—C8	124.4 (2)	O5—N4—C8	120.2 (2)
C12—C7—C8	111.6 (2)	O7—N5—O6	122.6 (2)
C9—C8—N4	115.8 (2)	O7—N5—C10	119.2 (2)
C9—C8—C7	124.1 (2)	O6—N5—C10	118.2 (2)
N4—C8—C7	120.2 (2)	O8—N6—O9	121.8 (2)
C8—C9—C10	119.5 (2)	O8—N6—C12	118.6 (2)
C8—C9—H9	120.3	O9—N6—C12	119.6 (2)
C10—C9—H9	120.3	C7—O3—H10A	134.2 (9)
C9—C10—C11	121.5 (2)	H1B—O10—H10B	108 (3)
C9—C10—N5	119.5 (2)	H1B—O10—H10A	114 (2)
C11—C10—N5	119.0 (2)	H10B—O10—H10A	110.2 (17)
C12—C11—C10	119.2 (2)		
N2—C1—C2—C3	-177.3 (3)	C8—C7—C12—C11	3.9 (3)
C6—C1—C2—C3	-0.4 (4)	O3—C7—C12—N6	4.4 (4)
C1—C2—C3—C4	0.1 (4)	C8—C7—C12—N6	-177.02 (19)
C2—C3—C4—C5	0.5 (4)	C2—C1—N2—N1	-24.1 (4)
C2—C3—C4—N3	-178.4 (2)	C6—C1—N2—N1	159.0 (3)
C3—C4—C5—C6	-0.7 (4)	C3—C4—N3—O1	3.9 (4)
N3—C4—C5—C6	178.3 (3)	C5—C4—N3—O1	-175.0 (3)
C4—C5—C6—C1	0.3 (4)	C3—C4—N3—O2	-177.1 (3)
N2—C1—C6—C5	177.3 (3)	C5—C4—N3—O2	3.9 (4)
C2—C1—C6—C5	0.3 (4)	C9—C8—N4—O4	-178.5 (3)
O3—C7—C8—C9	174.6 (2)	C7—C8—N4—O4	0.1 (4)
C12—C7—C8—C9	-3.9 (3)	C9—C8—N4—O5	1.5 (4)
O3—C7—C8—N4	-3.9 (4)	C7—C8—N4—O5	-179.9 (3)
C12—C7—C8—N4	177.60 (19)	C9—C10—N5—O7	-175.1 (2)
N4—C8—C9—C10	-179.9 (2)	C11—C10—N5—O7	6.1 (3)
C7—C8—C9—C10	1.5 (3)	C9—C10—N5—O6	6.8 (3)
C8—C9—C10—C11	1.3 (3)	C11—C10—N5—O6	-172.1 (2)
C8—C9—C10—N5	-177.5 (2)	C11—C12—N6—O8	11.2 (3)
C9—C10—C11—C12	-1.3 (3)	C7—C12—N6—O8	-167.9 (2)
N5—C10—C11—C12	177.5 (2)	C11—C12—N6—O9	-167.3 (2)
C10—C11—C12—C7	-1.6 (3)	C7—C12—N6—O9	13.6 (3)
C10—C11—C12—N6	179.32 (19)	C12—C7—O3—H10A	155.2 (11)
O3—C7—C12—C11	-174.6 (2)	C8—C7—O3—H10A	-23.2 (12)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1A...O10 ⁱ	0.87 (1)	2.05 (1)	2.916 (3)	177 (2)
N1—H1B...O10	0.87 (1)	1.94 (1)	2.809 (3)	172 (2)
N1—H1B...O9 ⁱⁱ	0.87 (1)	2.56 (3)	2.908 (3)	105 (2)
N1—H1C...O6 ⁱⁱⁱ	0.87 (1)	2.08 (1)	2.947 (3)	170 (2)
N2—H2A...O4	0.86 (1)	2.13 (2)	2.868 (3)	144 (3)
O10—H10A...O3	0.82 (1)	2.09 (2)	2.832 (3)	150 (3)
O10—H10A...O4	0.82 (1)	2.24 (2)	2.743 (3)	120 (2)

O10—H10B···O3 ⁱⁱ	0.83 (1)	2.05 (1)	2.869 (3)	171 (3)
O10—H10B···O9 ⁱⁱ	0.83 (1)	2.43 (3)	2.898 (3)	117 (3)
C11—H11···O8 ^{iv}	0.93	2.51	3.433 (3)	172

Symmetry codes: (i) $x-1, y, z$; (ii) $-x+1, -y+1, -z+1$; (iii) $x-1, y, z-1$; (iv) $-x+3, -y+1, -z+2$.